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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification: C09J 123/26, 123/16	A1	(11) International Publication Number: WO 95/10575 (43) International Publication Date: 20 April 1995 (20.04.95)
(21) International Application Number: PCT/US94/11576 (22) International Filing Date: 12 October 1994 (12.10.94) (30) Priority Data: 08/135,691 13 October 1993 (13.10.93) US (71) Applicant: EXXON CHEMICAL PATENTS INC. [US/US]; 5200 Bayway Drive, Baytown, TX 77520 (US). (72) Inventors: ROBERTSON, Martha, Hetzel; Route 2, Box 169, Zachary, LA 70791 (US). McELRATH, Kenneth, Odell, Jr.; 19515 Suncove Lane, Humble, TX 77346 (US). PABST, Mary, Joann; 1506 Country Club, Crosby, TX 77532 (US). (74) Agents: BELL, Catherine, L. et al.; Exxon Chemical Company, P.O. Box 2149, Baytown, TX 77522-2149 (US).		(81) Designated States: CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: ADHESIVES FROM LOW MOLECULAR WEIGHT POLYPROPYLENE (57) Abstract This invention relates to hot melt adhesives having Mw/Mn's of 5 or less comprising tackifier and semi-crystalline random homopolymers of propylene or copolymers of propylene and up to 28 weight percent of an α -olefin, preferably ethylene, treated with a peroxide or other agent to reduce the melt viscosity.		

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**TITLE: ADHESIVES FROM LOW MOLECULAR WEIGHT
POLYPROPYLENE**

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This application is a continuation-in-part of
copending U.S. Serial No. 08/135,691 filed October 13,
1993.

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FIELD OF THE INVENTION

This invention relates to hot melt adhesives based
upon semi-crystalline polypropylene which has been
subjected to controlled rheology and blended with a
tackifier. This invention further relates to a process
for using the adhesive.

BACKGROUND OF THE INVENTION

25

It has long been recognized that polypropylene
(PP) can be used as a polyolefin base in hot melt
adhesive (HMA) compositions. However, despite very
attractive economics, the utility of the various types
of polypropylene (atactic, crystalline or semi-
crystalline) has been limited by several serious
shortcomings. Semi-crystalline polypropylene based hot
melts tend to be somewhat brittle and have high
viscosities which prohibit their use in standard melt
processing equipment utilized by the industry. Also
the required application temperatures are so high for
crystallin PP hot melts, that polyolefin substrate
surfaces ar distorted at the application temperatures.
Hot melts based on atactic polypropylen on th other
hand tend to have low temperature resistance and lack
cohesive str ngth.

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It has also long been known that applying "controlled rheology" or "CRing" to a polymer, i.e., molecular weight reduction via peroxide or other degradation, is an excellent route to viscosity reduction for random co-polymers of polypropylene. Typically, polypropylene has not been subjected to controlled rheology to the degree that would reduce molecular weight sufficiently for utility in adhesives.

10

The most commonly used polymers for hot melt adhesives are ethylene vinyl acetate copolymers (EVA) and styrenic block copolymers, such as styrene-isoprene-styrene and styrene-butadiene-styrene triblocks. Styrenic block copolymers are composed of plastic end blocks called domains which act as crosslinks between the ends of the non-polar rubbery chains. These end blocks serve to lock the rubbery chains and their inherent entanglements in place. The high temperature resistance of these copolymers is determined by the glass transition temperature (T_g) of the end block which typically falls in the range of 80° to 95°C. Above the T_g of the plastic phase, the end blocks soften and cease to crosslink the end blocks which effectively destroys the cohesive strength of the adhesive.

20

EVA's are semi-crystalline materials characterized by crystalline ethylene domains conducted by poly amorphous regions. All the vinyl acetate resides in amorphous regions. Crystallinity is broken by random vinyl acetate punctuations along the chains. It is these crystalline domains which impart cohesive strength to the adhesive. As the level of vinyl acetate is increased, the EVA polymer becomes less and less crystalline and the melt temperature (T_m) decreases accordingly. The upper service temperature

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f adhesives based on these materials is limited to the melt temperature (T_m) of the crystalline domains. EVA based hot melt adhesives begin to lose their bond integrity at temperatures approaching the melt temperature of the polymer. The melt temperature of EVA typically ranges from 60° to 85°C depending on the vinyl acetate content.

Isotactic polypropylene homopolymer is a highly crystalline, high modulus material with a melt temperature near 165°C. The amorphous regions in polypropylene homopolymer typically comprise approximately 30% amorphous material which can be tackified to provide adhesive character to an HMA of polypropylene homopolymer. This is much less than the amorphous regions in EVA's used in hot melt adhesives. In random copolymers of polypropylene (RCP), however, crystallinity is broken up by random ethylene punctuations which provide a larger amorphous region to tackify. This also decreases the melt temperature of the crystalline regions to the range of 130° to 145°C. In these RCP's the crystalline domains impart cohesive strength to the adhesive blend and also increase stiffness. In addition, RCP has a non-polar amorphous phase which is more compatible with non-polar hydrocarbon tackifiers. Blends of these RCP's and non-polar tackifiers bond more strongly with non-polar low energy surfaces such as polypropylene.

U.S. Patent 4,105,718 discloses a process reacting a blend of a substantially amorphous polyolefin and a hydrocarbon rubber blend with peroxide at high temperatures to provide permanently tacky, low viscosity material useful in pressure sensitive adhesives. Similarly, U.S. Patent 4,749,739 discloses a hot melt adhesive composition capable of bonding paper to metal, glass and polyethylene comprising

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amorphous polypropylene, a hydrocarbon tackifier resin, a rosin tackifier and wax. Likewise, Canadian Patent 999698 discloses a composition containing atactic polypropylene and tackifier. Japanese Kokai J55048-236
5 discloses a hot melt sealant composition produced by reacting an elastomer and non-crystalline polypropylene or a mixture of non-crystalline polypropylene and crystalline polypropylene with organic peroxides and thereafter adding tackifiers. Japanese Kokai 55069-637
10 discloses a mixture of non-crystalline polyolefin, elastomer, organic peroxide and optionally tackifier. Japanese Kokai 1144483 discloses an HMA comprising styrenic thermoplastic rubber, tackifier, oil and low molecular weight polypropylene. U.S. Patent 3,798,118
15 discloses a mixture of high melt flow crystalline polypropylene and amorphous polypropylene. Most of the above compositions suffer from the deficiency of utilizing amorphous or atactic polypropylene which is known to have low cohesive strength and low temperature
20 resistance. These blends compensate for the low cohesive strength of the polypropylene by blending in an elastomer to provide strength. Canadian 999,698 and U.S. 4,749,739 disclose the use of amorphous polypropylene or atactic polypropylene and tackifier.
25 Thus, it is desirable that a polypropylene based hot melt adhesive having good cohesive strength without the addition of elastomer be developed. Further it is desirable that a propylene HMA be developed that does not require the use of amorphous polypropylene for
30 tackification.

The instant invention meets these objectives.

BRIEF DESCRIPTION OF THE FIGURES

35 Figure 1 is the GPC trace of the blended polypropylenes in blend B in Table 7.

- 5 -

Figure 2 is the GPC trace of the CR'ed polypropylene in blend A in Table 7.

Figure 3 is the GPC trace of Exxon PD 9298 prior to "CRing".

SUMMARY OF THE INVENTION

This invention relates to a composition comprising semi-crystalline random copolymers of propylene and up to about 30 wt.% of a C₁ to C₂₀ α -olefin, preferably C₁ to C₆, even more preferably ethylene, having a melt flow rate (MFR) of greater than or equal to about 2, preferably greater than or equal to about 30, preferably greater than or equal to about 75 as measured by ASTM D1238-90b, blended with tackifier. These adhesives are especially useful for polyolefin substrates, particularly in high temperature applications.

DESCRIPTION OF PREFERRED EMBODIMENTS

Hot melt adhesives are defined by ASTM D-907-91b as "an adhesive which is rendered fluid by heat and forms a bond upon cooling". A hot melt adhesive may be applied in the molten state, as a powder or as a dry film and the like. Preferred hot melt adhesives of this invention comprise a polymer having a melt flow rate (MFR) of 75 or greater which provides cohesive strength and high and low temperature performance and a tackifying resin which decreases viscosity and shifts blend T_g to help improve adhesion and wetting. The compositions may contain a wax which lowers viscosity and cost. Fillers and antioxidants known to those of ordinary skill in the art as well as other additives can also be utilized.

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A preferred polymer, polypropylene having an MFR of 75 or greater, is subjected to controlled rheology, (CR'ed polypropylene). Preferred polypropylenes are random copolymers of polypropylene and an alpha olefin wherein the alpha olefin comprises up to 28 wt.% of the copolymer, preferably at least 5 wt.% of the copolymer, even more preferably 5 to 10 wt.% of the copolymer, based upon the weight of the copolymer. The alpha olefin may be any C₂ to C₂₀ alpha olefin, preferably C₂ to C₈, even more preferably, ethylene, butene and/or hexene. Preferred embodiments comprise random copolymers of propylene and ethylene, butene and/or hexene. Particularly preferred propylene polymers are semi-crystalline. In a preferred embodiment, the propylene polymer is semi-crystalline and preferably substantially free of amorphous polypropylene. For purposes of this invention and the claims thereto, substantially free of amorphous polypropylene shall mean having 10% or less extractables, preferably 7 % or less extractables as measured by exposing the resin to n-hexane at 50°C for two hours, as further described in 21 CFR 177.1520(d)(3)(ii), which is incorporated by reference herein. In addition, semi-crystalline shall mean having about 50% or more crystallinity, preferably about 70% or more, as measured by DSC using a reference heat of fusion from a homopolymer of polypropylene. Likewise, in a preferred embodiment the propylene copolymer preferably has a heat of fusion as measured by DSC of about 90 J/g or more, even more preferably about 95 J/g or more. In preferred formulations the adhesive composition is essentially free of elastomer. By essentially free of elastomer is meant less than 3 % by weight of elastomer, based upon the weight of the composition. Preferred polypropylenes are isotactic polypropylenes.

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Prior to being subjected to controlled rheology the propylene polymer may have any weight average molecular weight or MFR as long as the final propylene polymer product has the desired MFR, of 2 to 500, preferably 10 to 250, even more preferably 30 to 100. The degree of "CR'ing" or molecular weight reduction is typically reported in terms of MFR. (Melt Flow Rate as measured by ASTM D-1238-90b). For a particular polymer, the higher the MFR, the more CR'ing that has been done to produce a corresponding low viscosity. After "CR'ing" the polymer preferably has a narrow molecular weight distribution (M_w/M_n) characterized by unimodal peaks. In a preferred embodiment the M_w fractions are semi-crystalline and substantially free of amorphous polypropylene. Typically the M_w/M_n is less than or equal to 5, preferably less than or equal to 4.

The polypropylene is then subjected to controlled rheology or other forms of degradation which are known methods for reducing viscosity and molecular weight of a polymer. This can be done in an extruder, a batch reactor or other any other appropriate receptacle where the polypropylene is contacted with a degradation agent, such as a catalyst, a peroxide or other free radical source. The conditions for use of a controlled rheology agent, such as peroxide, are within the skill of one of ordinary skill in the art who can take into consideration the temperature of the controlled rheology process and the half life of the particular agent used.

Peroxides are preferred controlled rheology agents. Examples of useful peroxides include but are not limited to di-*t*-butyl diperphthalate; *t*-butyl peracetate; *t*-butyl peroxy malic acid; 1-hydroxy-1-hydroperoxy dicyclohexyl peroxide; *t*-butyl perbenzoate;

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n-butyl-4,4-bis (t-butyl peroxy) valerate; bis (1-hydroxycyclohexyl) peroxide dicumyl peroxide, 2,5-dimethyl-2,5-bis(t-butyl peroxy) hexane; methylethyl ketone peroxides; 2,5-bis(t-butyl peroxy) 2,5-dimethylhexane bisperoxides; di-t-butyl peroxide; 2,5-dimethyl-2,5-bis(t-butyl peroxy) hexyne-3; ketone peroxides; pinane hydroperoxide; 2,5-dimethyl hexane-2,5-dihydroperoxide; cumene hydroperoxides and another suitable organic peroxides known to those of ordinary skill in the art. These peroxides may be used in pure form or compounded with suitable diluents such as inert organic solvents or inorganic carriers. Neat peroxides are preferred.

The amount of any chosen peroxide or other agent to be used in the treatment of a given polymer is dependent upon the weight of the polymer to be treated and the extent to which viscosity must be reduced. In general it has been found that the amount of peroxide will be from about 0.01 parts by weight peroxide compound to about two parts by weight per one hundred parts by weight of the polymer. From about 0.05 to about 0.5 parts by weight peroxide are preferred. The temperature of the controlled rheology process is primarily a function of the rheology of the polymer which is to be treated. The peroxide or agent must be dispersed in the polymer and the temperature of the process will always be at least as high as the melting point of the polymer and is as much above the melting point as necessary to obtain reasonably good agitation of the polymer. With most polymers, this is within the range of from about 100° to about 250°C preferably 150° to about 220°C even more preferably 170° to 190°C. It is preferred to use as low a temperature as possible, consistent with ease of agitation, to avoid undesirable degradation of the polymer. Preferably, the temperature of the process is initially 10° to 50°C

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above the softening point of the polymer or polymer mixture to be treated.

The propylene polymer may be blended with
5 tackifiers, before or after the CR'ing process. Other additives known to those of ordinary skill in the art may also be added to the composition at the appropriate times. The polymer is typically present in the blend at from about 5 to about 95% by weight based upon the
10 weight of the blend and the tackifier is present at about 95 to about 5 weight percent based upon the weight of the blend. The treated polymer is preferably present from about 30 to about 80 wt.% even more preferably about 40 to about 60 wt.% with the tackifier
15 being present at about 20 to about 70 wt.%, preferably about 40 to about 60 wt.%.

Tackifiers which can be used in this invention include one or more of: natural linear, cyclic or
20 branched hydrocarbon resins, synthetic linear, cyclic, or branched hydrocarbon resins and naturally occurring resins, such as terpene resins, rosin resins, rosin esters, tall oil esters, aliphatic hydrocarbons or mixtures thereof. Tackifiers which can be used in this
25 invention include one or more of the natural hydrocarbon resins, synthetic hydrocarbon resins and naturally occurring resins, such as terpene resins, rosin esters, tall oil esters, and aliphatic hydrocarbon resins prepared by the polymerization of
30 monomers consisting primarily of olefins and diolefins and hydrogenated forms of these resins. Examples include those grades marketed by Exxon Chemical Company such as Escorez 1310LC® and ECR-143H®. Further tackifiers include the hydrocarbon products of the
35 distillation of petroleum oil, particularly hydrogenated cyclic resins with a Tg of -14° to 70°C and a ring and ball softening point of 18° to 130°C.

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Examples include Exxon Chemical Co.'s Escorez 5380®, Escorez 5320®, and ECR-327®. Mixtures of these tackifiers can also be used.

5 Preferred hot melt adhesives of this invention are characterized by good cohesive strength, high temperature resistance and outstanding adhesion to polyolefins; particularly polypropylene. Polypropylene is a surface known to be difficult to bond adhesively
10 due to its inherently low surface energy and its lack of polar functionality. In a preferred embodiment the adhesive composition is characterized by a peel strength of at least about 2.5 lbs/in (0.45 kg/cm) on a polyolefin surface, preferably a polypropylene surface.
15 In a particularly preferred embodiment the adhesive composition is characterized by a peel strength of at least about 3.0 lbs/in (0.54 kg/cm) on a polyolefin surface, preferably a polypropylene surface.

20 Other additives and fillers may be added to the blend such as for example carbon black, antioxidants, antistatics, blowing agents, viscosity modifiers, colorants, fillers, clay, silica, talc and the like.

25 In a preferred embodiment the hot melt adhesive compositions described above further comprise wax which is present at 5 to 40 weight percent, preferably 10 to 30 weight percent, based upon the weight of the composition.

30 In another preferred embodiment, the final adhesive composition has a melt viscosity, as measured by a Brookfield viscometer, of 2 to 150 poise, preferably 5 to 50 poise, and preferably have a melt
35 index as measured by ASTM D 1238-90b, Condition E of at least about 300 gm/10 min.

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In another preferred embodiment the final adhesive composition has a peel strength on polyolefin substrates, preferably polypropylene, of at least about 2.5 pounds per inch (0.45 kg/cm), preferably at least about 3.0 pounds per inch (0.54 kg/cm). Further preferred final adhesive compositions have a shear adhesion failure temperature (SAFT) of at least about 100 °C, preferably at least about 130 °C.

In general, viscosity is inversely related to MFR's (the higher the viscosity, the lower the MFR). The relationship is not a linear relationship, however, because viscosity is impacted by a whole host of parameters such as blend compatibility, branching, crosslinking, etc. Melt Flow Rates are typically run on neat polymers whereas viscosities are usually reported for blends.

EXAMPLES

In the examples below, various blends of semi-crystalline random polypropylene co-polymers containing 5 or 9.8% ethylene were blended with various tackifiers. The compositions are listed in the table below.

TABLE I

	Polymer 1-RCP (5 mol% ethylene, 2.9 MFR)
30	Polymer 2-RCP (5 mol% ethylene, 31 MFR)
	Polymer 3-RCP (5 mol% ethylene, 79 MFR)
	Polymer 4-RCP (9.8 mol% ethylene,)

Tackifier 1 hydrogenated aliphatic liquid tackifier, Tg=-21°C, Mw=532, Mn=301, MWD=1.77, available as ECR 143H™ from Exxon Chemical Company, Baton Rouge, La.

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Tackifier 2 was a hydrogenated aliphatic hydrocarbon resin $T_g=29.4^{\circ}\text{C}$, available as ECR-111TM from Exxon Chemical Company, Baton Rouge, La.

5

Tackifier 3 is a cyclic hydrogenated liquid aliphatic resin, $T_g=-13.4^{\circ}\text{C}$, $M_w=165$, $M_n=76$, $MWD=2.17$, available as ECR-327TM from Exxon Chemical Company, Baton Rouge, La.

10

Tackifier 4 is a hydrogenated hydrocarbon resin, $T_g=\text{approximatley } 30^{\circ}\text{C}$, $M_w=420$, $M_n=320$, $MWD=1.3$, available as ESCOREZ 5380TM from Exxon Chemical Company, Baton Rouge, La.

15

All the formulations were melt blended at 180°C and mixed in a mantel heated beaker using a high torque mechanical mixer except for a few of the very high viscosity systems which were blended in a Z-blade mixer. In all cases the mixing chamber was nitrogen blanketed to reduce oxidative degradation. In blending these HMA's in a beaker, a portion of the tackifier was placed in the beaker and allowed to become molten. The polymer and the remaining tackifier was then added alternately and incrementally. When all ingredients were completely added the blends were allowed to mix for approximately ten minutes to ensure homogeneity. The blends were then poured on silicone lined release paper and allowed to cool to room temperature prior to testing.

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25
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T-peel, lapsh ar, SAFT specimens were prepared using drawn films made in the following way: preheated adhesive (about 150°C) was poured onto silicone lined release coated paper and hand-drawn to produce a thin adhesive film of 5 to 6 mil. using an 8 path applicator from Gardner Laboratory. Once cooled these films wer

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cut into strips. Bonds were made by sandwiching these strips of adhesives between two substrates and heating the adhesives until molten either in a heated barsealer or an oven. T-Peel samples were bonded in peel configuration with a bonded area of 1" X 3". Samples were bonded using a heated barsealer. Various times, temperature and pressure conditions for sealing were evaluated and are disclosed in Table 1. All T-Peel measurements were done at a separation speed of 2 in./min. Samples were tested at temperatures ranging from 23°C to 75°C.

SAFT samples were bonded in the same manner as T-Peel specimens in lapshear configuration with a 1" x 1" area overlap. They were run on both Kraft paper and polypropylene substrates. SAFT samples are placed in a 90°F oven which is computer programmed to automatically increase the oven temperature at 0.67°F per minute. A 500 gm weight is typically hung on the lower end of the sample; however in many of our tests we had to increase the weight to 1 kilogram in order to achieve failure below the maximum oven temperature of 141°C. The temperature at which the bond fails is recorded as the SAFT value.

Lapshear samples were made by placing a 1" square of the dry adhesive on a 1" x 4" substrate coupon and heating in a mechanical convection oven for 3 minutes at a 150°C. After 3 minutes the coupon with adhesive was removed from the oven and another room temperature coupon was placed on the molten adhesive in lapshear configuration to make the bond. The bond was clamped in place until the adhesive cooled to room temperature and set. Tensile specimens were die cut from hydraulically pressed pads of each HMA blend. 75 mil pads were molded between the silicone lined release paper at a 150°C for approximately 15 minutes. All

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samples were pulled on an Instron tensile tester. Cross head speed was 2" per minute. Dynamic mechanical experiments were performed using a DMTA. Each sample was scanned -100 to 150°C at a ramp rate of 4°C per minute and a frequency of 1 Hz. Samples were tested in dual cantilever bending mode or in shear mode.

Example 1.

10 In the peroxide degradation below, a blend of a cyclic hydrogenated tackifier (60 weight%) and 2 melt flow rate (MFR) random co-polymer polypropylene (40 wt%) were melt blended in a Z-blade mixer until homogeneous. The blend was poured onto silicone
15 release paper and allowed to solidify and cool to room temperature. A portion of the blended material was placed in dry ice for approximately 4 hours until very brittle. At this point the blend was pounded to break it into very small pieces. A 10% by weight solution of
20 Lupersol 101 [2,5 dimethyl-2,5-bis(t-butylperoxyl)hexane] in pentane was mixed. The small polymer blend pieces were then slurried in the peroxide solution in a beaker which was open to the air. The peroxide was added at the level of 2 weight based on
25 the weight of only the RCP in the blend. After most of the pentane evaporated, the beaker was placed in a heating mantle and slowly heated with stirring from room temperature to 150°C. As the temperature increased, the degradation reaction began to occur and
30 some yellowing was seen. The reaction was continued through 5 half-lives of the peroxide. The degraded blend was then poured on silicone release paper and allowed to cool to room temperature. Brookfield viscosity and Melt Index, as measured by ASTM D 1238-
35 90b Condition E, were run on both the original blend and the degraded blend. Those data appear in Table 2.

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Table 2

	<u>Original Blend</u>	<u>Degraded Blend</u>
Brookfield Viscosity, cps	>500,000 @ 200C	32,600 @ 175C
Melt Index (gm/10 min)	45.5	558
(Flow time @ 190C)	18.02 sec.	1.47 sec.

Example 2.

10

These data are disclosed in Table 3. Random copolymer polypropylene (2 MFR) and 2 CR'ed versions of this material (31 MFR and 75 MFR) were melt blended with a 29°C Tg hydrogenated aliphatic tackifier in a 1:1 ratio by weight. A similar blend was made with an amorphous polypropylene copolymer. These adhesive blends were evaluated side by side for peel strength to polypropylene substrates, shear adhesion failure temperature (SAFT), and Brookfield viscosity. These data clearly indicate the superior performance of the semi-crystalline RCP blends over the amorphous PP blend both in room temperature peel properties and in elevated temperature shear properties. It is also clear from these data that reducing blend viscosity greater than ten fold (>500,000 to 50,000 cps) via CR'ing has a surprisingly negligible negative impact on peel and shear (SAFT) properties.

30

TABLE 3

	Amorphous PP Copolymer	2MFR RCP	31MFR RCP	75MFR RCP
T-Peel (1) (lbs/in)	12.9	>25(sf)	24.8	19.5(sf)
(kg/cm)	(2.30)	(4.46)	(4.41)	(3.48)
SAFT (2) (°C)	87.5	>141	140	132
Brookfield Viscosity (3) (poise)	1.9	500	106.3	50

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- (1) on Polypropylene @25°C
 - (2) Shear adhesion fail temperature 1" x 1" x 1 kg, (except amorphous PP Copol was tested with a 0.5 kg weight).
 - 5 (3) @175°C
- sf = substrate failure

Example 3.

10 These data are disclosed in Table 4. The procedure of Example 2 was followed. The blend component and proportions are set out in Table 4. This example illustrates the superior bond strength of RCP-based HMA's versus both EVA and Polyethylene (PE) based
15 HMA's, particularly in higher service temperature applications. This example also illustrates that adhesive brittleness, which often can be a problem when polymer molecular weight is highly degraded, can be overcome by incorporating an additional low Tg
20 tackifier to modify blend glass transition temperature. Blends C and D, EVA and PE based HMA's respectively, exhibit peel strengths at room temperature (23°C) which are comparable to or lower than those of the RCP based blends (A and B) when peeled at 75°C. This
25 advantageous performance at higher temperature in the RCP blends is again due to the inherently higher melt temperature of RCP versus EVA and PE.

30 The low peel strength of Blend A at 23°C is due to brittle failure of the adhesive at that temperature. The very high peel strength of blend B at that temperature illustrates the value of a low Tg tackifier for modifying blend Tg and ultimately HMA performance.

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TABLE 4

Blend	A	B	C	D
Component				
EVA ⁽¹⁾			50	
5 PE ⁽²⁾				50
RCP ⁽³⁾	50	50		
Tackifier 1 ⁽⁴⁾			50	
Tackifier 2 ⁽⁵⁾				50
Tackifier 3 ⁽⁶⁾	50	25		
10 Tackifier 3 ⁽⁷⁾		25		
Irganox 1010 TM	0.5	0.5	0.5	0.5
T _m (°C) ⁽⁸⁾	130	128	--	--
T _g (°C) ⁽⁹⁾	48	38		
15 T-Peel (lbs/in) ⁽¹⁰⁾				
(kg/cm)				
Temp (°C)				
25	1.5A	19.9SF	4.5A	7.6A
	(0.27)	(3.55)	(0.80)	(1.36)
40	11NP	11.1NP	--	--
20 (1.96)	(1.96)	(1.98)	--	--
60	7.6NP	7.3NP	--	--
(1.36)	(1.36)	(1.30)	--	--
75	6.6NP	7.2NP	--	--
(1.18)	(1.18)	(1.29)		
25 (1) Ethylene/Vinyl acetate (28 weight % VA, 6MI). (2) An ethylene/butene copolymer available from Exxon Chemical Company under the trade name EXACT 4037 TM . (3) Random propylene/ethylene copolymer having a 75 MFR and 5 wt% ethylene. (4) Rosin ester. (5) Aliphatic hydrocarbon. (6) Hydrogenated cyclic, T _g = 30°C. (7) Hydrogenated cyclic, T _g = -14°C. (8) DSC melting point. (9) as measured by DSC. (10) on polypropylene. A=adhesive failure, NP= no peel, SF=substrate failure. (To convert lbs/in to kg/cm multiply lb/in by 0.1785.)				
35 Irganox 1010 TM = tetrakis(methylene(3,5-di-tert-butyl-4-hydroxyhydrocinamate)).				

Example 5.

40 The polymers from Example 2 were blended with various tackifiers according to the procedure in Example 2. The data are presented in Tables 5A and 5B.

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TABLE 5A

Polymer		A	B	C	D	E	F
1 - RCP (2MFR)		50	50	-	-	-	-
2 -RCP (31MFR)		-	-	-	-	-	-
3 -RCP (75MFR)		-	-	-	50	50	50
4 - RCP		-	-	50	-	-	-
Tackifier							
1 (143H)		-	-	-	-	-	-
2 (111)		50	25	50	-	50	25
3 (327)		-	25	-	-	-	25
4 (5380)		-	-	-	50	-	-
Irganox 1010		-	-	-	0.5	0.5	0.5
Brookfield Viscosity @ 175C		500 p	53 p	63.4 p		50 p	
T-Peel (kg/cm)							
Substrate T (°C)							
PP 23		0.36A	2.53C	2.10C	0.27A	0.36A	2.54C
PP 34		-	-	-	2.30C	2.28C	-
PP 40		1.88C	1.71C	0.39C	1.96NP	1.87C	1.71C
PP 60		0.66C	1.03C	0.13C	1.36NP	0.66C	1.04C
PP 75		0.52C	0.59C	0.06C	1.07NP	0.52C	0.59C
PE 23				1.51C			
Al 23		0.07A	0.11A	1.05A			
T-Peel (lb/in)							
Substrate T (°C)							
PP 23		1.99A	14.16C	11.74C	1.5A	2.0A	14.2C
PP 34		-	-	-	12.9C	12.8C	-
PP 40		10.52C	9.62C	2.21C	11.0NP	10.5C	9.6C
PP 60		3.7C	5.75C	0.7C	7.6NP	3.7C	5.8C
PP 75		2.9C	3.3C	0.34C	6.0NP	2.9C	3.3C
PE 23				8.45C			
Al 23		0.38A	0.62A	5.9A			
DSC Tm °C					129.6	130.7	128.3
DMTA Tg °C					48	38	24
SAFT °C/l"x1"x1kg		>141				132	

A= Adhesive failure; C= Cohesive failure; S= Substrate failure; NP= No Peel; C/A= Mixed Mode

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TABLE 5B

Polymer	G	H	J	K	L
1 - RCP (2MFR)	-	-	-	-	-
2 -RCP (31MFR)	-	-	-	-	50
3 -RCP (75MFR)	50	50	40	30	-
4 - RCP	-	-	-	-	-
Tackifier					
1 (143H)	25	-	-	-	-
2 (111)	25	-	60	70	50
3 (327)	-	25	-	-	-
4 (5380)	-	25	-	-	-
Irganox 1010	0.5	0.5	-	-	-
Brookfield Viscosity @ 175C			23.8 p	9.3 p	106 p
T-Peel (kg/cm)					
Substrate T (°C)					
PP 23	1.29C	3.52S	0.19	0.21	
PP 34	-	-	1.84C	1.60C	
PP 40	0.99C	1.98NP	1.55C	1.11C	
PP 60	0.45C	1.30C	0.74C	0.57C	
PP 75	0.45C	1.29NP	0.49C	0.41C	
PE 23					
Al 23					
T-Peel (lb/in)					
Substrate T (°C)					
PP 23	7.2C	19.7S	1.07	1.17	
PP 34	-	-	10.32C	8.98C	
PP 40	5.6C	11.1NP	8.77C	6.22C	
PP 60	2.5C	7.3C	4.12C	3.2C	
PP 75	2.5C	7.2NP	2.72C	2.28C	
PE 23					
Al 23					
DSC Tm °C	130.8	127.7			
DMTA Tg °C	-	37.5			
SAFT °C l"x1"x1kg					140

A= Adhesive failure; C= Cohesive failure; S= Substrate failure; NP= No Peel; C/A= Mixed Mode

5 Example 6.

Except as noted, the procedure of Example 2 was followed. The data are presented in Table 6.

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TABLE 6

		2MFR	31MFR	75MFR	EVA/PE
5	T-Peel on PP				
	(lbs/in)				
	(kg/cm)				
	Time ^a				
	Temp ^b				
	2	25	22.6C	22.1C	19.9C
			(4.03)	(3.95)	(3.55)
10	72	25	>25SF	24.8C	19.5SF 4.5/7.6
			(4.46)	(4.42)	(3.48) (.8/1.4)
	72	40	--	16.6	16.5
			--	(2.96)	(2.95)
	72	60	12.9	11.9	10.7
15			(2.30)	(2.12)	(1.91)
	72	75	10	11.6	7.1
			(1.79)	(2.07)	(1.27)
	SAFT (°C)		>141	140	132
	1" x 1" x 1kg				

20 a = post bonding time (hrs): b = peel temp. (°C);
 All samples bonded in an impulse heat sealer 3 seconds
 at 146 °C: C = cohesive failure; SF = substrate
 failure. EVA = EVA copolymer melt blended 1:1 with
 rosin ester tackifier. PE = copolymer of ethylene and
 25 butene melt blended 1:1 with ESCOREZ 1310LC, a C₅
 Tackifier available from Exxon Chemical Company.

The increase in peel strength and/or change in
 failure mode from cohesive to substrate failure as post
 30 bonding time increases from 2 to 72 hours is an
 indication of crystallization occurring. This would
 not occur in a HMA containing amorphous polymer. This
 build of crystallinity is what allows these blends to
 maintain high peel strength at these higher
 35 temperatures.

Comparative Example with U.S. 3,798,118

The following Examples were prepared according to
 40 the procedur in Example 1. The data and composition
 are reported in Table 7. Thes data show the superior
 abilities of the instantly claimed adhesive versus the
 adhesive pr sent in U.S. 3,798,118, even when the
 viscosities are similar.

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TABLE 7

	(U.S. 3,798,118) (Tbl. I, Blnd. F) Blend B	Blend A
Polypropylene (1)	25	--
CR'ed Polypropylene (2)	--	50
Amorphous Polypropylene (3)	50	--
Glycerol ester tackifier (4)	25	--
Hydrogenated Cyclic Tackifier (5)	--	25
Hydrogenated Cyclic Tackifier (6)	--	25
Antioxidant (7)	2	2
Melt viscosity @ 180°C, Cps (8)	55,300	55500
Shear Adhesion Fail Temp. °C (9)	60	106
T-Peel to polypropylene, lbs/in (10)	2.08 (CF) (0.37 kg/cm)	21.3 (CF) (3.8 kg/cm)
Mw/Mn	12.8	2.1

- 5 (1) Exxon PD 9282; 2 MI; 5 mol% ethylene
 (2) Exxon PD 9282 CR'ed to 75 MFR
 (3) Eastman propylene homopolymer D 7682-137
 (4) Anzona Chemical Zonester 85
 (5) Exxon Escorez 25380™
 10 (6) Exxon ECR-327
 (7) Irganox 1010™
 (8) Brookfield Viscometer Model RUT; #27 Spindle
 (9) 1" x 1" Lapshear bond; 1 kg. weight; Kraft
 Cardboard
 15 (10) Tensile tester crossbend speed 2"/minute
 (CF) Cohesive Failure

Likewise the GPC data show (Figures 1 and 2 are
 the GPC traces of the polypropylene incorporated in
 20 blends B and A, respectively) show the severe
 differences in Mw/Mn and modality. Figure 3 shows the
 GPC trace of the isotactic polypropylene prior to th
 CRing treatment.

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CLAIMS

We claim:

- 5 1. An adhesive composition comprising one or more tackifiers and semi-crystalline random propylene polymer having a melt flow rate (MFR) of 2 to 500 and having an Mw/Mn of 5 or less.
- 10 2. The composition of claim 1, wherein the propylene polymer comprises propylene and 5 to 15 weight percent of ethylene, hexene or butene.
- 15 3. The composition of claim 1 or 2, wherein the composition is substantially free of amorphous polypropylene.
- 20 4. The composition of claim 1, 2 or 3 characterized by a melt viscosity of 2 to 150 poise at 175°C.
5. The composition of any of the above claims wherein the tackifier is a hydrogenated tackifier.
- 25 6. The composition of any of the above claims characterized by a peel strength on a polyolefin substrate at 75°C of at least 0.45 kg/cm.
- 30 7. The composition of any of the above claims characterized by a shear adhesion failure temperature of at least 100°C.
8. The composition of any of the above claims wherein the Mw/Mn is 4 or less.
- 35 9. A process for producing hot melt adhesives having an Mw/Mn of 5 or less from semi-crystallin

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propylene polymers comprising: heating a propylene polymer to above the propylene polymer's softening point and combining the polypropylene polymer with one or more tackifiers and an agent in an amount sufficient to increase the melt index of the blend to at least about 300 gm/10min.

10. The process of claim 9 wherein the propylene polymer comprises propylene and 5 to 15 weight percent of ethylene, hexene or butene.

11. The process of claim 9 or 10, wherein the tackifier is a hydrogenated tackifier.

12. The process of claim 9, 10 or 11 wherein the agent is a peroxide.

13. A hot melt polypropylene adhesive substantially free of amorphous polypropylene produced by the steps comprising heating a semi-crystalline propylene polymer and one or more tackifiers to above the propylene polymer's softening point and adding an agent in an amount sufficient to increase the melt index of the blend to at least about 300 gm/10 min.

14. A hot melt polypropylene adhesive substantially free of amorphous polypropylene produced by the steps comprising heating a semi-crystalline propylene polymer to above the propylene polymer's softening point, adding an agent in an amount sufficient to increase the melt index of the blend to at least about 300 gm/10 min and thereafter adding one or more tackifiers.

15. The use of any of the compositions of claims 1 - 8 as a hot melt adhesive.

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16. An adhesive comprising:
a polymeric component consisting essentially
of semi-crystalline polypropylene; and
tackifier.

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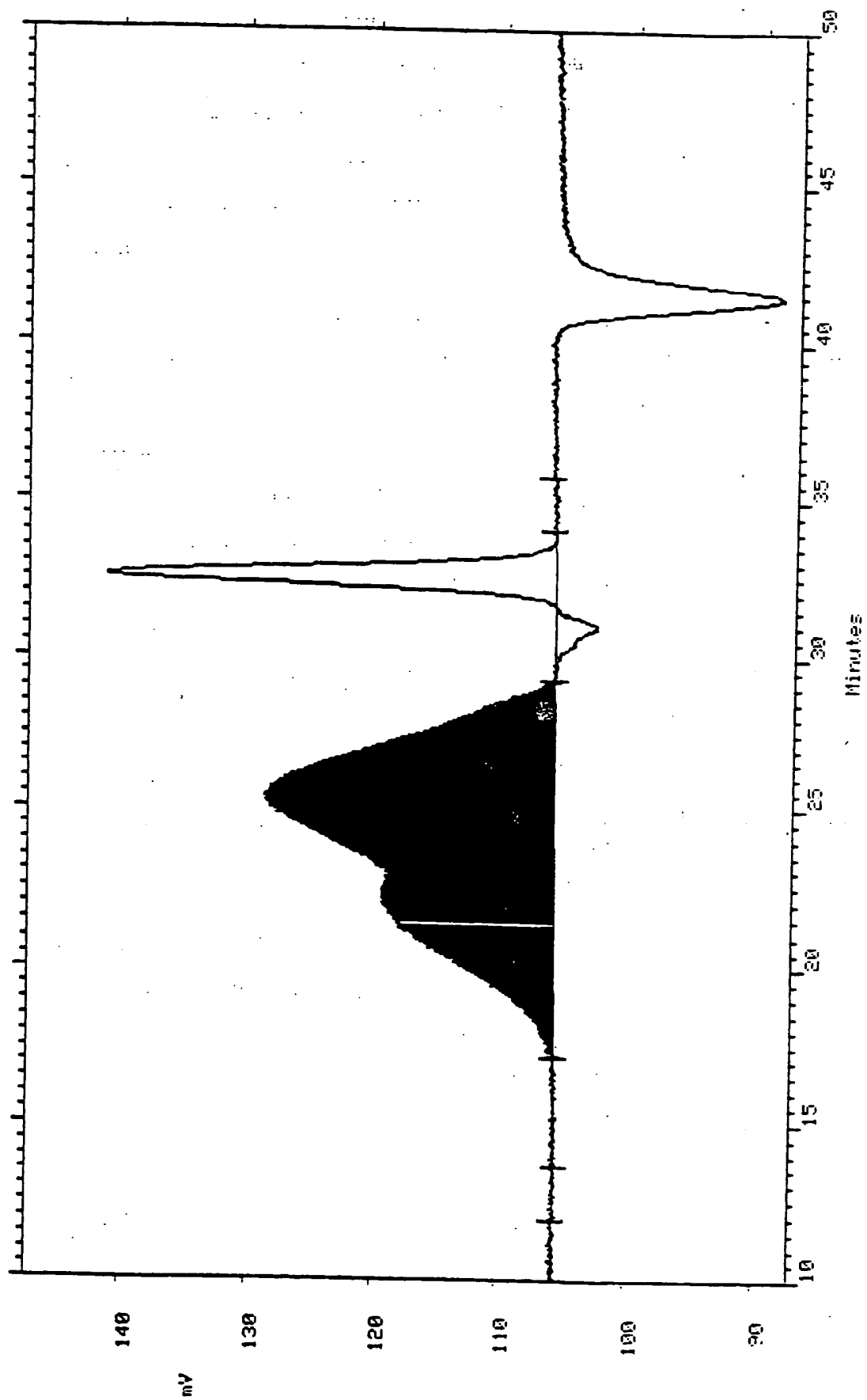
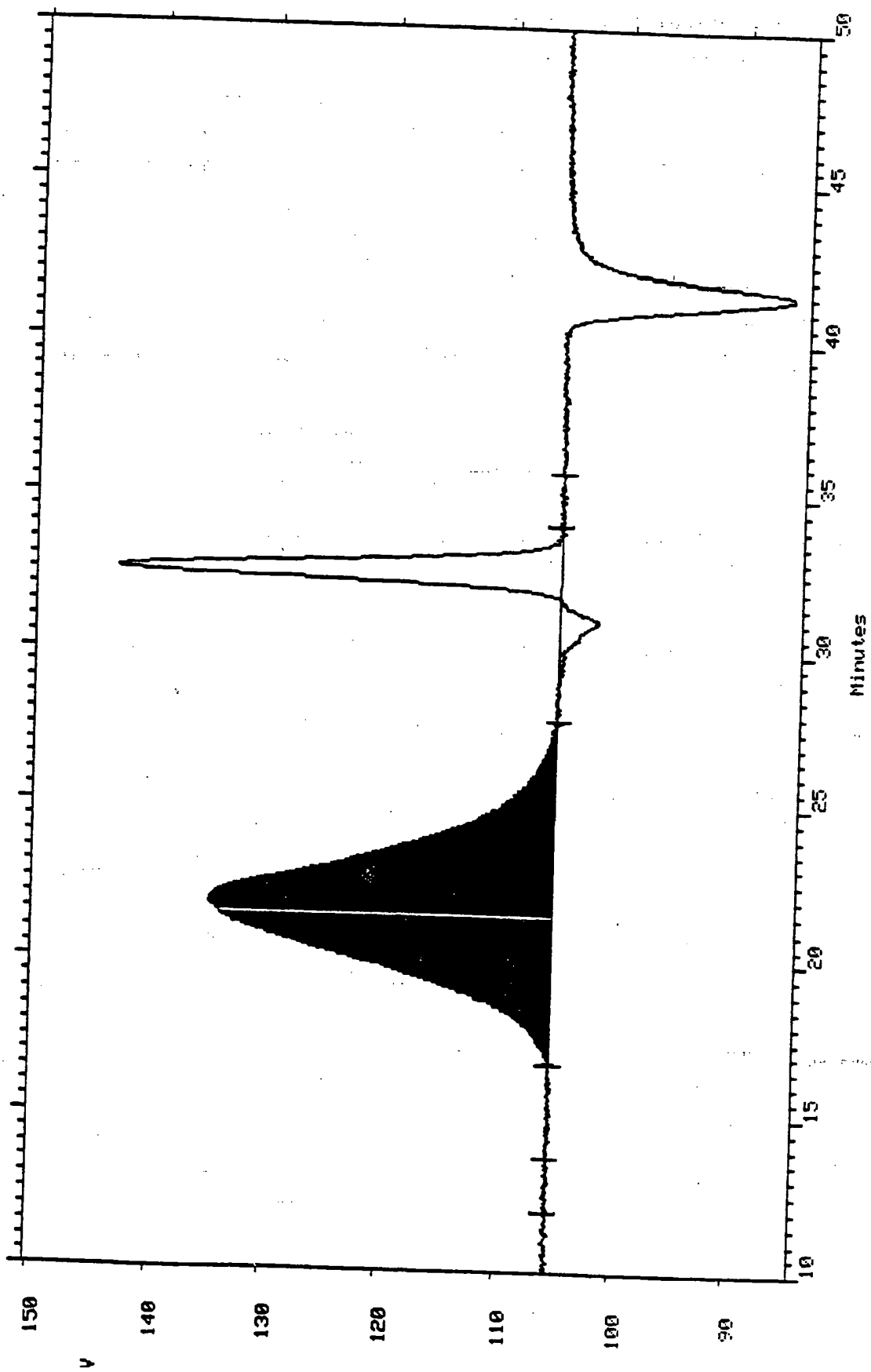


FIGURE 1

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**FIGURE 2**

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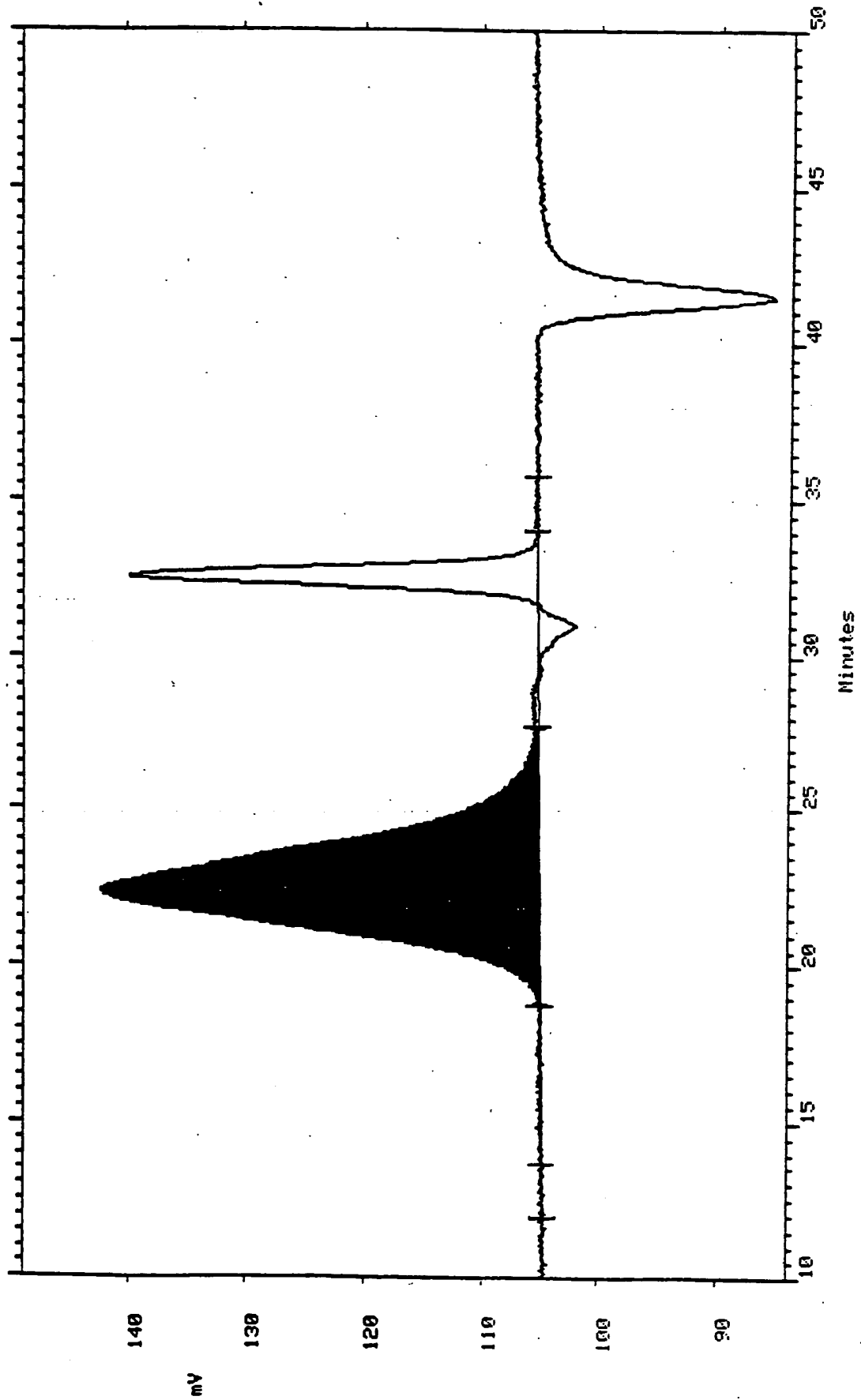


FIGURE 3

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 94/11576

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C09J123/26 C09J123/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09J C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CA,A,999 698 (REICHOLD CHEMICALS) 9 November 1976 cited in the application see the whole document ---	1-16
A	WO,A,79 00482 (EASTMAN KODAK) 26 July 1979 see page 1, line 25 - page 2, line 16 see page 3, line 1 - page 5, line 3 ---	1-16
A	US,A,4 528 312 (R.EDWARDS) 9 July 1985 see column 2, line 3 - column 3, line 2 see column 3, line 21 - column 4, line 59 --- -/--	1-16

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

7 February 1995

Date of mailing of the international search report

24. 02. 95

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax (+31-70) 340-3016

Authorized officer

Schmidt, H

C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Derwent Publications Ltd., London, GB; AN 91-299743 & JP,A,3 199 282 (MITSUI TOATSU) 30 August 1991 see abstract -----	1-16

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/US 94/11576

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CA-A-999698	09-11-76	NONE	
WO-A-7900482	26-07-79	US-A- 4210570	01-07-80
		CA-A- 1117681	02-02-82
		EP-A,B 0003194	25-07-79
US-A-4528312	09-07-85	NONE	